Oxocyano complexes of molybdenum(IV) and tungsten(IV) with Schiff base ligands derived from salicylaldehyde and aliphatic amines. Crystal structure of [PPh4]2[Mo(CN)3O(ensal)]·5.5H2O (Hensal = *N*-salicylideneethylenediamine)

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The reaction of $[M(CN)_4O(H_2O)]^{2-}$ (M = Mo) with salicylaldehyde and methylamine gave the complex $[Mo(CN)_3O(mesal)]^{2-}$, where Hmesal = *N*-salicylidenemethylamine. If ethylenediamine or propane-1,3-diamine is used in this type of reaction the complexes with singly condensed Schiff bases, *N*-salicylideneethylenediaminate (ensal) (M = Mo or W) or *N*-salicylidenepropane-1,3-diaminate (tnsal) (M = Mo), are obtained. X-Ray crystallographic analysis of $[PPh_4]_2[Mo(CN)_3O(ensal)]\cdot5.5H_2O$ showed that the 'half-unit' Schiff base co-ordinates in a bidentate manner with a non-coordinated NH_2 group. The complexes were characterised by elemental analysis, electronic absorption, IR and ^1H NMR spectra. The electronic absorption spectra show the presence of solvent dependent MLCT bands. Their solvatochromic effect is comparable with that observed for other complexes of similar structure.

Introduction

Schiff base complexes of molybdenum comprise a vast and diversified group of compounds. They attract particular interest as models for biochemical redox reactions which involve molybdenum ions.[1] The importance of Schiff bases is related to the common presence of a C=N bond in natural systems as well as to the fact that their easy formation gives the opportunity of building ligands of different structures. Furthermore, the co-ordination of Schiff base components may precede, and in some cases even enable, their condensation, which does not take place in aqueous media.[2] Hence it is possible to build ligands that do not exist as separate molecules.

In contrast to the great variety of compounds of Mo^V and Mo^{VI} described in the literature, examples of molybdenum(IV) Schiff base complexes are sparse. We have found that tetracyanodioxometalates (M = Mo or W) are good starting materials for synthesis of the complexes of Mo^{IV} and W^{IV} with Schiff base ligands. When $K_3Na[M(CN)_4O_2]\cdot6H_2O$ is dissolved in water one of the oxo ligands is protonated to OH^- and at lower pH to H_2O. The water molecule in $[M(CN)_4O(H_2O)]^{2-}$ is easily substituted and the reaction with monodentate ligands, such as F^-, SCN^-, N_3^-, CN^- or pyridine (py), leads to the formation of $[M(CN)_4O(L)]^{n-}$ complexes.[3] Bidentate ligands, like 2,2′-bipyridine (bpy),[4] 1,10-phenanthroline (phen)[5] or pyridine-2-carboxylate (pic),[6] replace water and one cyano ligand giving compounds of the formula $[M(CN)_3O(L–L)]^{n-}$. We have also observed formation of complexes of that type with bidentate Schiff bases derived from 2-acetylpyridine and methyl- or butyl-amine: $[M(CN)_3O(mesb)]^-$ or $[Mo(CN)_3O(busb)]^-$ {mesb = *N*-[1-(2-pyridyl)ethylidene]methylamine, busb = *N*-[1-(2-pyridyl)ethylidene]butylamine}.[7] There is one known example of incorporation of a tetradentate ligand, *N,N*′-bis[1-(2-pyridyl)ethylidene]ethylenediamine (ensb), in the reaction of $[Mo(CN)_4O(H_2O)]^{2-}$ with 2-acetylpyridine and ethylenediamine.[8] In this case water and two cyano ligands are substituted and the co-ordination number increases to seven, resulting in the neutral complex $[Mo(CN)_2O(ensb)]$.

The cyano complexes of Mo^{IV} and W^{IV} with organic ligands have found application in the study of solvation effects. Most of

these compounds are intensely coloured both in the solid state and in solution due to the presence of metal to ligand charge transfer (MLCT) transitions. The MLCT bands are usually strongly solvatochromic, and their maxima shift to shorter wavelengths on going from less to more polar solvents.[4,9–11] It was also found that some solvatochromic complexes of Mo and W show a piezochromic effect; a small shift of MLCT bands on application of high pressure.[11]

Herein we describe the solvent sensitivity of the singly condensed 'half-unit' Schiff base complexes **1**–**4**, and show that their solvatochromic effect is comparable with that observed for other complexes of similar structure.

Experimental

The complexes $K_3Na[M(CN)_4O_2]\cdot6H_2O$ (M = Mo or W)[12] and Schiff bases *N,N*′-bis(salicylidene)ethylenediamine and *N,N*′-bis(salicylidene)propane-1,3-diamine[13] were prepared by published methods. Other reagents and solvents of analytical purity were used as supplied. All solutions were prepared immediately before measurements.

Syntheses

Bis(tetraphenylphosphonium) tricyanooxo(*N*-salicylidenemethylaminato)molybdate(IV) dihydrate, $[PPh_4]_2[Mo(CN)_3O(mesal)]\cdot2H_2O$ 1. To an aqueous solution (40 ml) of $K_3Na[Mo(CN)_4O_2]\cdot6H_2O$ (0.5 mmol, 0.24 g), salicylaldehyde (4.7 mmol, 0.5 ml) in methanol (20 ml) and then methylamine (4 mmol, 0.5 ml of 25% aqueous solution) were added with stirring. The pH was adjusted to 8 with 0.1 mol dm^{-3} HCl. Then solid $[PPh_4]Cl$ (4 mmol, 1.50 g) was added and the mixture stirred for 15 min. The product usually separated from the solution as an oil and crystallised upon mixing. The resulting precipitate was filtered off, washed several times with water–methanol (3 : 1) and then with water and dried in air. Analytical data are given in Table 1.

Bis(tetraphenylphosphonium) tricyanooxo(*N*-salicylideneethylenediaminato)molybdate(IV)–water (2/1/5.5), $[PPh_4]_2[Mo(CN)_3O(ensal)]\cdot5.5H_2O$ 2. The salt $K_3Na[Mo(CN)_4O_2]\cdot6H_2O$

(0.5 mmol, 0.24 g) was dissolved in water (40 ml) and the pH of the solution adjusted to 7 with 0.1 mol dm^{-3} HCl. A methanolic solution (20 ml) of salicylaldehyde (5.7 mmol, 6 ml) and then ethylenediamine (3 mmol, 0.2 ml) were added. The pH was adjusted to 8 by dropwise addition of 0.1 mol dm^{-3} HCl and the mixture stirred for 30 min. The yellow crystals of *N,N'*-bis(salicylidene)ethylenediamine were filtered off. Solid [PPh$_4$]Cl (4 mmol, 1.5 g) was then added to the filtrate and the mixture treated as in the case of complex **1**.

Bis(tetraphenylphosphonium) **tricyanooxo(*N*-salicylidene-ethylenediaminato)tungstate(IV)–water (2/1/5.5), [PPh$_4$]$_2$[W(CN)$_3$O(ensal)]·5.5H$_2$O 3.** This was prepared like complex **2**, but the reactants were kept at 50 °C for 1 h before the excess of Schiff base was removed.

Bis(tetraphenylphosphonium) **tricyanooxo(*N*-salicylidene-propane-1,3-diaminato)molybdate(IV)–water (2/1/5.5), [PPh$_4$]$_2$-[Mo(CN)$_3$O(tnsal)]·5.5H$_2$O 4.** This was obtained in a similar manner to complex **2**, using propane-1,3-diamine (3 mmol, 0.25 ml).

Tungsten analogues of **1** and **4** were not obtained due to problems with isolation of pure products.

Analytical methods and physical measurements

Carbon, nitrogen and hydrogen were determined by organic microanalysis. The content of water was determined by thermogravimetric analysis (TG). These analyses as well as differential thermal analysis (DTA) were performed under argon within the temperature range 25–250 °C, with a heating rate of 2 °C min^{-1} on a MOM-Q 1500 thermoanalyser (Hungary). The UV/VIS absorption spectra were measured on a Shimadzu 2101 PC spectrometer under argon, immediately after preparation of solutions, ESR spectra on a Se/X-25 (Poland) at room temperature, ^{1}H NMR spectra on a Bruker AMX-500 spectrometer in (CD$_3$)$_2$SO under argon and IR spectra in KBr pellets on a Bruker IFS 48 spectrometer.

Crystal structure determination of complex 2

Crystal data and data collection parameters. C$_{60}$H$_{51}$MoN$_5$O$_2$-P$_2$·5.5H$_2$O, $M = 1131.03$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.384(5)$, $b = 14.309(3)$, $c = 17.745(5)$ Å, $\alpha = 69.38(2)$, $\beta = 73.90(4)$, $\gamma = 82.67(3)°$, $V = 2826(2)$ Å^3 (by least-squares refinement on diffractometer angles from 20 centred reflections, $4.7 \leqslant 2\theta \leqslant 22.0°$), $T = 200$ K, $Z = 2$, $D_c = 1.329$ Mg m^{-3}, $F(000) = 1178$, green block with dimensions $0.40 \times 0.20 \times 0.15$ mm, μ(Mo-Kα) = 0.346 mm^{-1}, graphite monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, Siemens P4 diffractometer, ω scans with variable scan speed (4.0–40.0° min^{-1}), data collection range $4.1 \leqslant 2\theta \leqslant 55.4°$, three standard reflections showed no significant variation in intensity; no absorption correction, 10644 reflections measured, 9451 unique ($R_{int} = 0.0625$) of which 9450 were used in all calculations.

Structure solution and refinement. The structure was solved by direct methods and subsequent Fourier-difference techniques, full-matrix least squares refinement on F^2 (SHELXTL 5.03).[14] Owing to the poor diffracting power of the crystal, there was only a small number of 'observed' reflections. Therefore, only the heavier atoms (Mo and P) were refined anisotropically, while all other non-hydrogen atoms were refined with isotropic displacement parameters. The hydrogen atoms were calculated in idealised positions and allowed to ride on their corresponding C and N atoms, their isotropic thermal parameters being tied to those of the adjacent atoms by a factor of 1.5. No H atoms were included for the solvate water molecules. The weighting scheme was $w = 1/[\sigma^2(F^2) + (0.0879P)^2]$, $P = (F_o^2 + 2F_c^2)/3$. The final $wR2(F^2)$ was 0.2465, with conventional $R1(F)$ 0.0949 [$F_o \geqslant 4\sigma(F)$] for 321 parameters and 0 restraints, goodness of fit = 0.884, maximum $\Delta/\sigma = 0.002$, maximum $\Delta\rho = 0.688$, minimum $\Delta\rho = -0.940$ e Å^{-3}

CCDC reference number 186/1204.

See http://www.rsc.org/suppdata/dt/1998/4009/ for crystallographic files in .cif format.

Results and discussion

Reaction of [Mo(CN)$_4$O(H$_2$O)]$^{2-}$ with salicylaldehyde and amines

When a methanolic solution of salicylaldehyde is added to a neutral aqueous solution of [Mo(CN)$_4$O(H$_2$O)]$^{2-}$ the originally blue colour of the latter changes to green as a result of the co-ordination of the aldehyde.[15] After addition of methylamine a relatively stable compound is formed, which can be isolated as a tetraphenylphosphonium salt. Elemental analysis of the product coincides with the formula [PPh$_4$]$_2$[Mo(CN)$_3$-O(mesal)]·2H$_2$O **1**, where mesal is the deprotonated Schiff base *N*-salicylidenemethylamine.
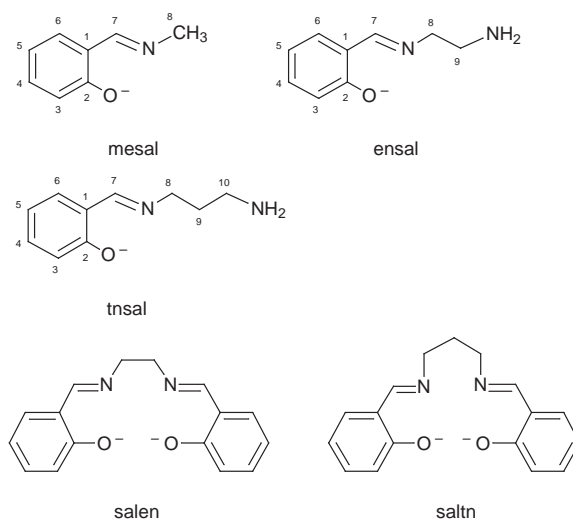
mesal   ensal   tnsal   salen   saltn

The reaction of aquatetracyanooxometalates(IV) with salicylaldehyde and ethylenediamine or propane-1,3-diamine is hindered by the precipitation of the Schiff bases *N,N'*-bis(salicylidene)ethylenediamine (H$_2$salen) or *N,N'*-bis(salicylidene)propane-1,3-diamine (H$_2$saltn), which are insoluble in water–methanol mixtures. After removing the solid from the green filtrate the resulting complexes were isolated by addition of [PPh$_4$]Cl. It was expected that the reaction should lead to the complexes with symmetrical tetradentate ligands salen and saltn. However, the products were found to contain singly condensed 'half-unit' Schiff bases *N*-salicylideneethylenediaminate (ensal) and *N*-salicylidenepropane-1,3-diaminate (tnsal). Complexes of the following formulae have been obtained: [PPh$_4$][Mo(CN)$_3$O(ensal)]·5.5H$_2$O **2**, [PPh$_4$]$_2$-[W(CN)$_3$O(ensal)]· 5.5H$_2$O **3** and [PPh$_4$]$_2$[Mo(CN)$_3$O(tnsal)]· 5.5H$_2$O **4**. The structure of **2** was confirmed by X-ray analysis. The 'half-unit' complexes do not react with an excess of salicylaldehyde even at longer times and higher temperature. We have also performed a two-phase reaction between [Mo(CN)$_4$O(H$_2$O)]$^{2-}$ in water and H$_2$salen in toluene, but again the 'half-unit' Schiff base complex **2** was obtained in very low yield.

Compounds **1**–**4** are green solids, ESR inactive, consistent with a spin paired d^2 configuration. They are soluble in polar organic solvents such as alcohols, acetonitrile, acetone or dmso and insoluble in water and non-polar solvents. In solution they decompose within a few minutes even in darkness and under argon. Slowest decomposition was observed in dmso, and it was used for recording NMR spectra.

Table 1 Analytical[a] and physical data

| Complex | Yield (%) | IR/cm^{-1} | | | Analysis (%) | | |
		$\nu(C\equiv N)$	$\nu(M=O)$	Schiff base	C	H	N
1 $[PPh_4]_2[Mo(CN)_3O(mesal)]\cdot 2H_2O$	34.6	2088m	932s	903w, 1318w, 1474m, 1542w	68.20 (68.21)	4.99 (5.04)	5.42 (5.39)
2 $[PPh_4]_2[Mo(CN)_3O(ensal)]\cdot 5.5H_2O$	38.9	2088s, 2102 (sh)	933m	908m, 1318m, 1472m, 1545w	64.09 (63.71)	5.44 (5.53)	5.97 (6.19)
3 $[PPh_4]_2[W(CN)_3O(ensal)]\cdot 5.5H_2O$	26.3	2077s, 2100w	936m	905m, 1310m, 1471m, 1540w	59.12 (59.12)	4.99 (5.13)	5.27 (5.75)
4 $[PPh_4]_2[Mo(CN)_3O(tnsal)]\cdot 5.5H_2O$	36.7	2095s, 2108vw	932s	901w, 1323m, 1469m, 1545w	63.77 (63.98)	5.45 (5.63)	5.67 (6.12)

[a] Required values are given in parentheses.

Table 2 Selected bond lengths (Å) and angles (°) for $[PPh_4]_2[Mo(CN)_3O(ensal)]\cdot 5.5H_2O$ **2**

Mo(1)–O(2)	1.699(7)	C(4)–C(5)	1.49(1)
Mo(1)–O(3)	2.069(7)	C(5)–N(5)	1.47(1)
Mo(1)–C(1)	2.13(1)	C(11)–C(12)	1.42(1)
Mo(1)–C(2)	2.18(1)	C(12)–C(13)	1.40(1)
Mo(1)–C(3)	2.05(1)	C(13)–C(14)	1.39(1)
Mo(1)–N(4)	2.171(8)	C(14)–C(15)	1.39(1)
C(1)–N(1)	1.19(1)	C(15)–C(16)	1.39(1)
C(2)–N(2)	1.17(1)	C(11)–C(16)	1.42(1)
C(3)–N(3)	1.20(1)	C(12)–C(17)	1.43(1)
O(3)–C(11)	1.32(1)	N(4)–C(17)	1.32(1)
N(4)–C(4)	1.51(1)		
O(2)–Mo(1)–C(1)	97.0(4)	C(2)–Mo(1)–C(3)	168.2(4)
O(2)–Mo(1)–C(2)	95.4(4)	C(1)–Mo(1)–N(4)	169.5(3)
O(2)–Mo(1)–C(3)	96.5(4)	Mo(1)–C(1)–N(1)	172.6(8)
O(2)–Mo(1)–N(4)	93.3(3)	Mo(1)–C(2)–N(2)	178.0(9)
O(3)–Mo(1)–C(1)	86.8(4)	Mo(1)–C(3)–N(3)	175.1(10)
O(3)–Mo(1)–C(2)	83.9(3)	Mo(1)–O(3)–C(11)	135.0(6)
O(3)–Mo(1)–C(3)	84.2(4)	Mo(1)–N(4)–C(17)	128.4(8)
O(3)–Mo(1)–N(4)	82.9(3)	Mo(1)–N(4)–C(4)	117.6(7)
C(1)–Mo(1)–C(2)	91.9(4)	N(4)–C(4)–C(5)	110.4(9)
C(1)–Mo(1)–C(3)	86.8(4)	C(4)–C(5)–N(5)	113.2(11)
C(2)–Mo(1)–N(4)	89.3(3)	N(4)–C(17)–C(12)	126.0(10)
C(3)–Mo(1)–N(4)	89.8(4)	O(3)–C(11)–C(12)	122.0(10)
O(2)–Mo(1)–O(3)	176.1(3)	C(11)–C(12)–C(17)	124.5(10)

Fig. 1 Structure of $[Mo(CN)_3O(ensal)]^{2-}$ anion in complex **2**.

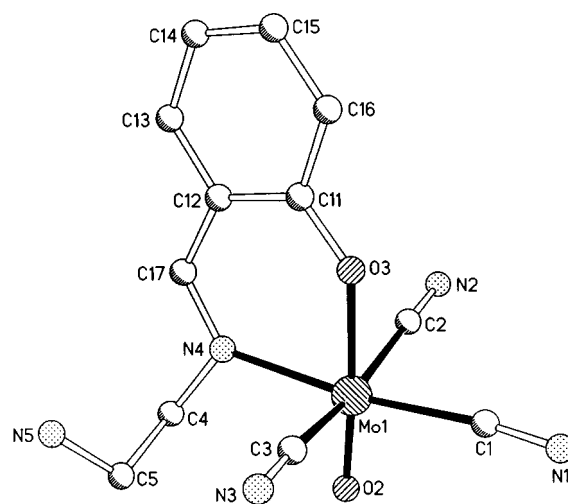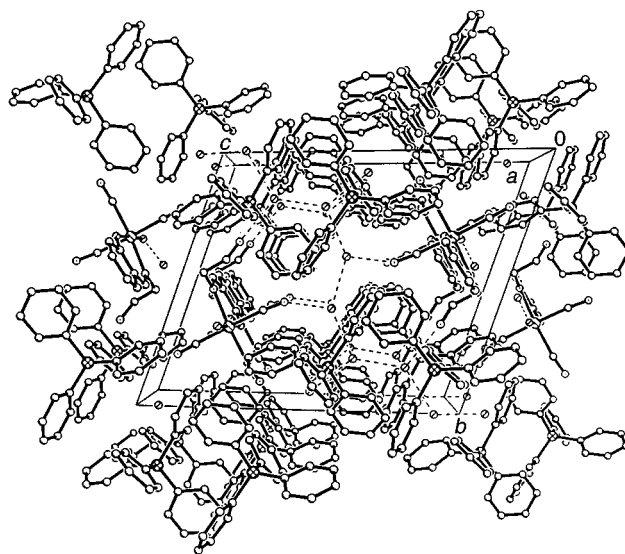**Fig. 2** Structure of $[PPh_4]_2[Mo(CN)_3O(ensal)]\cdot 5.5H_2O$ **2**.

Structure of $[PPh_4]_2[Mo(CN)_3O(ensal)]\cdot 5.5H_2O$ 2

Selected bond lengths and angles are presented in Table 2. The structure of complex **2** shows clearly that in the reaction of $[Mo(CN)_4O(H_2O)]^{2-}$ with salicylaldehyde and ethylenediamine the 'half-unit' Schiff base, *N*-salicylideneethylenediamine, is formed (Fig. 1). It co-ordinates in a bidentate manner through the deprotonated OH group and imine nitrogen, which gives a six-membered chelate ring. The NH$_2$ group is not bonded to the metal, sticking out of the complex. The molybdenum ion is bonded to three cyano groups and the oxo ligand. The immediate metal environment shows distorted octahedral geometry with both oxygen atoms in axial positions and the cyano groups and imine nitrogen in the equatorial plane. The Mo atom is significantly displaced from that plane towards the oxo ligand by 0.205(5) Å, as in other complexes of this type, $[Mo(CN)_3$-$O(bpy)]^{-4}$ and $[Mo(CN)_3O(phen)]^{-}$.[5] The Mo–C≡N chains are slightly bent with an average deviation from 180° of 4.8°.

The cations and anions in the structure of complex **2** are arranged in separate columns along the *x* axis (Fig. 2). The water molecules, linked *via* hydrogen bonds with cyano and oxo ligands and the amine group of ensal, form layers cutting through cation stacks in the *yz* plane.

NMR spectra

The ^{1}H NMR spectra of complexes **1–4** (Table 3) consist of the resonances of PPh$_4^+$ cation and respective Schiff base ligand. The signals of the amine aliphatic chain protons can be observed in the region δ 2.2–4.1, while aldehyde ring and side

chain protons peaks appear at δ 6.2–7.4. Comparison of their integrals indicates 1 : 1 aldehyde : amine ratios in all complexes, which is in agreement with the assumed ligand formulae. The non-symmetrical character of diamine bonding in **2**, **3** and **4** is shown by the splitting of amine chain signals into two triplets (H8 and H9) for **2** and **3** or two triplets (H8 and H10) and a multiplet (H9) for **4**. The spectra of the symmetrical Schiff bases H$_2$salen and H$_2$saltn consist of one singlet (H8 + H9) or one triplet (H8 + H10) and a multiplet (H9), respectively (Table 3). It is noted that the positions of salicylaldehyde signals are independent of the structure of the Schiff base, but are strongly influenced by co-ordination. They are identical for all the

Table 3 Proton NMR spectral data of $[PPh_4]_2[Mo(CN)_3O(mesal)]\cdot2H_2O$ **1**, $[PPh_4]_2[Mo(CN)_3O(ensal)]\cdot5.5H_2O$ **2**, $[PPh_4]_2[W(CN)_3O(ensal)]\cdot5.5H_2O$ **3** and $[PPh_4]_2[Mo(CN)_3O(tnsal)]\cdot5.5H_2O$ **4** in comparison with N,N'-bis(salicylidene)ethylenediamine (H_2salen) and N,N'-bis(salicylidene)propane-1,3-diamine (H_2saltn): chemical shift (δ), multiplicity,[a] coupling constant (Hz), relative integrated intensity

H_2salen	H_2saltn	1	2	3	4	Assignment
	2.02qnt, 6.8 (2)		3.24t, 5.6 (2)	3.32t, 5.9 (2)	2.22m (2)	H9
[b]					2.63t, 6.7 (2)	H10
	[c]	3.38s	3.36s	3.37s	3.37s	H_2O
3.92s (4)	3.68t, 6.8 (4)	3.91s (3)	3.98t, 5.5 (2)	4.01t, 5.5 (2)	4.06t, 7.0 (2)	H8
6.89m (4)	6.89m (4)	6.17d, 8.4 (1)	6.18d, 8.3 (1)	6.39d, 8.2 (1)	6.17d, 8.4 (1)	H3
		6.43t, 7.3 (1)	6.44t, 7.3 (1)	6.56t, 7.3 (1)	6.42t, 7.6 (1)	H5
7.32t, 7.8 (2)	7.33t, 7.8 (2)	6.90t, 7.7 (1)	6.90t, 7.7 (1)	6.68t, 7.7 (1)	6.90m (1)	H4
7.43d, 7.6 (2)	7.44d, 7.5 (2)	7.13d, 7.7 (1)	7.14d, 7.7 (1)	7.00d, 7.7 (1)	7.13m (1)	H6
				7.32s (1)		H7
		7.74m (16)	7.74m (6)	7.74m (16)	7.74m (16)	
		7.82m (16)	7.82m (16)	7.82m (16)	7.82m (16)	cation
		7.97m (8)	7.97m (8)	7.97m (8)	7.97m (8)	
8.59s (2)	8.59s (2)	8.24s (1)	8.21s (1)		8.21s (1)	H7
13.53s (2)	13.53s (2)					OH

[a] s = Singlet, d = doublet, t = triplet, qnt = quintet, m = multiplet. [b] One peak for H8 + H9. [c] One peak for H8 + H10.
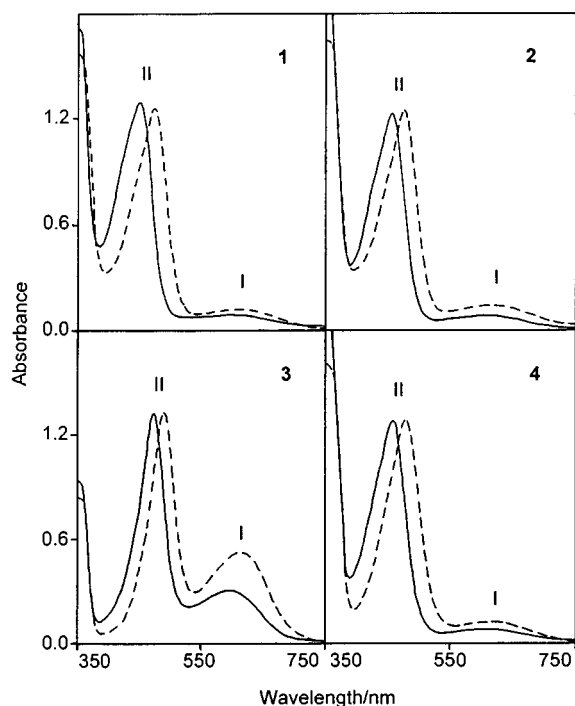
Fig. 3 Electronic absorption spectra of $[PPh_4]_2[Mo(CN)_3O(mesal)]\cdot2H_2O$ **1**, $[PPh_4]_2[Mo(CN)_3O(ensal)]\cdot5.5H_2O$ **2**, $[PPh_4]_2[W(CN)_3O(ensal)]\cdot5.5H_2O$ **3** and $[PPh_4]_2[Mo(CN)_3O(tnsal)]\cdot5.5H_2O$ **4** in methanol (solid line) and acetonitrile (broken line).

molybdenum complexes but different for the tungsten complex and both free Schiff bases. The aromatic ring signals shift upfield by an average 0.5 ppm upon co-ordination. The hydrogen of the imine carbon is even more affected as its resonance in the molybdenum complexes (**1**, **2**, **4**) and in the tungsten complex (**3**) appears 0.4 and 1.3 ppm lower, respectively, compared to those of the non-co-ordinated Schiff bases. The absence of the OH signal in the spectra of **1**–**4**, which for H_2salen and H_2saltn appears at δ 13.5, is consistent with the deprotonation of the hydroxyl group.

Solvatochromism

The electronic absorption spectra of complexes **1**–**4** (Fig. 3) in the visible region are dominated by MLCT bands, the positions and intensities of which depend on the nature of the solvent. The band maxima shift to shorter wavelengths with increasing polarity of the solvent (Table 4), which is connected with donor–acceptor interactions and hydrogen bond formation

Table 4 Electronic absorption spectral data of complexes **1**–**4**

Solvent (E_T/kcal mol^{-1})	1	2	3	4
Methanol	319	323	355	321
(55.5)	449	456	472	456
	598	603	597	604
Ethanol	320	324	357	321
(51.9)	456	461	478	461
	602	609	603	607
Butan-1-ol	—	—	—	320
(50.2)	470	470	486	472
	611	611	615	610
Propan-2-ol	320	324	359	319
(48.6)	463	470	487	471
	607	613	617	608
Acetonitrile	356	356	360	357
(46.0)	473	475	490	476
	610	615	615	614
dmso	—	362	—	359
(45.0)	486	492	500	490
	626	639	639	630
dmf	359	364	—	364
(43.8)	497	497	506	499
	633	635	645	636
Acetone	—	365	—	364
(42.0)	498	498	506	499
	633	635	645	635

between ligands and solvent. The most intense MLCT band (II) shows the strongest solvatochromism. Similarly to solvatochromic cyano and carbonyl complexes of Fe, Mo and W with organic ligands,[9,11,16] a plot of ν_{max} of the band II for complexes **1**–**4** *versus* E_T (an experimentally determined position for the MLCT band of an organic dye in a given solvent, as described in ref. 17) consists of two straight lines of different slopes for hydroxylic and non-hydroxylic solvents.

We compared the solvatochromic effect of complexes **1**–**4** with those of other $[Mo(CN)_3O(L-L)]^{n-}$ complexes studied previously,[4,7,11] taking as the reference compound $[Mo(CN)_3O(bpy)]^-$[4] (Fig. 4). For all complexes a linear correlation was observed with slopes equal to 1.30 (**1**), 1.10 (**2**), 0.84 (**3**) and 1.14 (**4**). Combining these results with corresponding data for molybdenum(IV) and tungsten(IV) complexes with L–L = phen,[11] mesb or busb,[7] we established the increasing order of the solvatochromic effect: $[W(CN)_3O(mesb)]^- < [W(CN)_3O(bpy)]^- < [Mo(CN)_3O(busb)]^- \leqslant [Mo(CN)_3O(mesb)]^- < [W(CN)_3O(ensal)]^{2-} < [Mo(CN)_3O(bpy)]^- < [Mo(CN)_3O(phen)]^- < [Mo(CN)_3O(ensal)]^{2-} \leqslant [Mo(CN)_3O(tnsal)]^{2-} < [Mo(CN)_3O(mesal)]^{2-}$. It is noticeable that in pairs of molybdenum and tungsten compounds of the same structure tungsten complexes are significantly less solvatochromic.
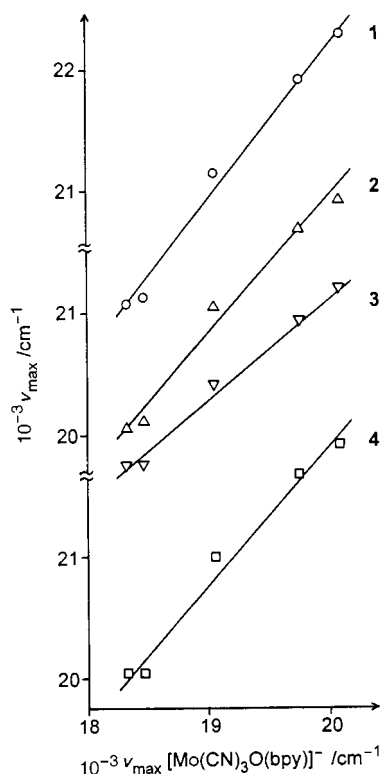
Fig. 4 Solvatochromic effect of band II of complexes **1**, **2**, **3** and **4** in comparison to that of the corresponding band of [Mo(CN)₃O(bpy)]⁻.

Conclusion

It was found that the reaction of aquatetracyanooxomolybdate(IV) with salicylaldehyde and methylamine results in the Schiff base complex $[Mo(CN)_3O(mesal)]^{2-}$ **1**. Analogous reactions with ethylenediamine and propane-1,3-diamine lead to the formation of the complexes with singly condensed 'half-unit' Schiff bases. The crystal structure of $[PPh_4]_2[Mo(CN)_3O$-$(ensal)]\cdot 5.5H_2O$ **2** showed that *N*-salicylideneethylenediamine acts as a bidentate ligand with a non-co-ordinated NH_2 group.

Structural data give some information on the mechanism of Schiff base ligand formation on the metal centre. In $[Mo(CN)_4$-$O_2]^{4-}$ the oxo ligands are situated in *trans* position. In the structure of complex **2** the position *trans* to the oxo ligand is occupied by the O^- atom of salicylaldehyde. Assuming that the configuration around the Mo is retained during reaction, as was found for substitution of monodentate ligands,[18] the deprotonated hydroxyl group of salicylaldehyde replaces water in $[Mo(CN)_4O(H_2O)]^{2-}$ and forms the first bond of the incoming organic ligand.

The fact that the reaction of aquatetracyanooxometalates(IV) with salicylaldehyde and diamines stops at the stage of singly condensed Schiff bases and that the complexes decompose in solution is probably connected with weak bonding of the deprotonated OH group to the metal. It was established that the stability constants of complexes of the type $[Mo(CN)_3$-$O(L–L)]^{n-}$ are much higher for bidentate ligands with two nitrogen donor atoms (bpy, 380 M⁻¹;[19] phen, 560 M⁻¹[20]) than for those with one oxygen and one nitrogen (pic, 13 M⁻¹[6]). This difference seems to account for the formation of 'half unit' ligands from salicylaldehyde and diamines, while the reaction with 2-acetylpyridine and ethylenediamine gives a tetradentate symmetrical Schiff base complex.[8] The presence of a six-membered chelate ring, less stable than the five-membered one, may also contribute to these effects.

The formation of Schiff base 'half-units' is rather rare. In some cases single condensation can be achieved *via* organic synthesis from diluted solutions with high amine:aldehyde/ketone

ratio, however it was shown that 'half-units' derived from salicylaldehyde and ethylenediamine or propane-1,3-diamine cannot be obtained in that way.[21] There are only a few examples of complexes with ensal[22] and tnsal[23] ligands, none of them with Mo or W as central atom. All these complexes were obtained in template reactions or by transfer of the ligand from another complex. The novelty of our complexes is the bidentate mode of co-ordination of 'half-unit' Schiff bases. In all known complexes ensal and tnsal are tridentate ligands with amine nitrogen as a third donor atom. To the best of our knowledge there is no previous example of an ensal or tnsal complex with a non-co-ordinated NH_2 group.

'Half-units' are important from the point of view of the synthesis of non-symmetrical Schiff bases derived from a diamine and two different aldehydes/ketones.[21] Even though the complexes **2**–**4** are unstable in solution they may potentially react with some aldehydes or ketones which co-ordinate to Mo^{IV} or W^{IV}. It also seems possible that the 'half-unit' complexes can act as 'ligand donors' in reaction with other metals.

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